Studies on Pyrrhotite. II : The First Decreasing Change in Weight

Studies on Pyrrhotite. II

"The First Decreasing Change in Weight"*

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Synopsis

The mechanism of "the first decreasing change in weight", that is, the vigorous decrease in weight taking place temporarily at about 405°C in the course of heating the fine particles of native pyrrhotite was discussed from the analysis of the roasting reaction of pyrrhotite and the characteristics of heating curves of artificial pyrrhotite containing various amounts of sulphur. It was clarified that this phenomenon was caused by the deflagration of the structural component FeS_2 contained in the native pyrrhotite. The deflagration of the component FeS_2 led to the reaction of oxide formation of the component FeS and the decomposition of the sulphate formed at low temperatures. The magnitude of "the first decreasing change in weight" was, therefore, larger than the decrease in weight resulting from the oxidation of the component FeS_2. Furthermore, the effects of mixing pyrite on the combustibility of pyrrhotite was investigated. By pyrite mixing, the ignitibility and the reaction rate of oxide formation of ores were considerably increased. By mixing with 40～50 per cent of pyrite, pyrrhotite may become roastable under almost the same condition as in the case of pyrite roasting.

I. Introduction

"The first decreasing change in weight", that is, the vigorous decrease in weight taking place temporarily at about 405°C in the course of heating the fine particles of native pyrrhotite at a constant flow rate of air and a constant heating rate is an anomalous phenomenon. As mentioned in the previous report[1], the intensity of this phenomenon is associated closely with the ignitibility or the combustibility of pyrrhotite. To utilize pyrrhotite in industry as a source either of iron or of sulphur, it is, therefore, necessary to understand precisely the mechanism of "the first decreasing change in whight". Hence, in the present work, the mechanism was investigated in detail and, furthermore, the roasting method of native pyrrhotite was discussed.

II. Analysis of heating curve of pyrrhotite

"The first decreasing change in weight" was already found by H. Saito[2], who explained the mechanism as follows: the sintering of ore particles begins at 405°C, by which the reaction of sulphate formation is obstructed and only that of oxide formation goes on, and so the weight of particles remarkably decreases.

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* The 743rd report of the Research Institute for Iron, Steel and Other Metals.

(1) M. Maruyama, Sci. Rep. RITU, A **5** (1953), 208.

(2) H. Saito, J. Min. Inst. Japan, **41** (1925), 726.

According to the present author's opinion, however, this explamation seems to be unappropriate. In Fig. 1, the full line shows the change in weight taking place in the course of roasting pyrrhotite produced at the Ômine mine. When it is suposed that both the reaction of oxide formation and that of sulphate formation inactively progressed up to 405°C as indicated respectively by A_0 and A_s lines, they should progress respectively along A_0' and A_s' lines above 405°C in compliance with Saito's opinion. The change in weight of the ore will, therefore, be shown by P line, the sum of A_0' and A_s' lines. It does not, however, accord with "the first decreasing change in weight". Hence, the occurrence of "the first decreasing change in weight" will be inconceivable without supposing either the phenomenon shown by A_0'' line, the activation of the reaction of oxide formation, or that shown by A_s'' line, the decomposition of the sulphate. The sulphate is, however, stable at temperatures below 550°C, and so the phenomenon shown by A_s'' line is inconceivable. Consequently, it may be concluded that "the first decreasing change in weight" is due to the activation of the reaction of oxide formation. In short, it will be hard to explain this phenomenon only by the sintering of ore particles.

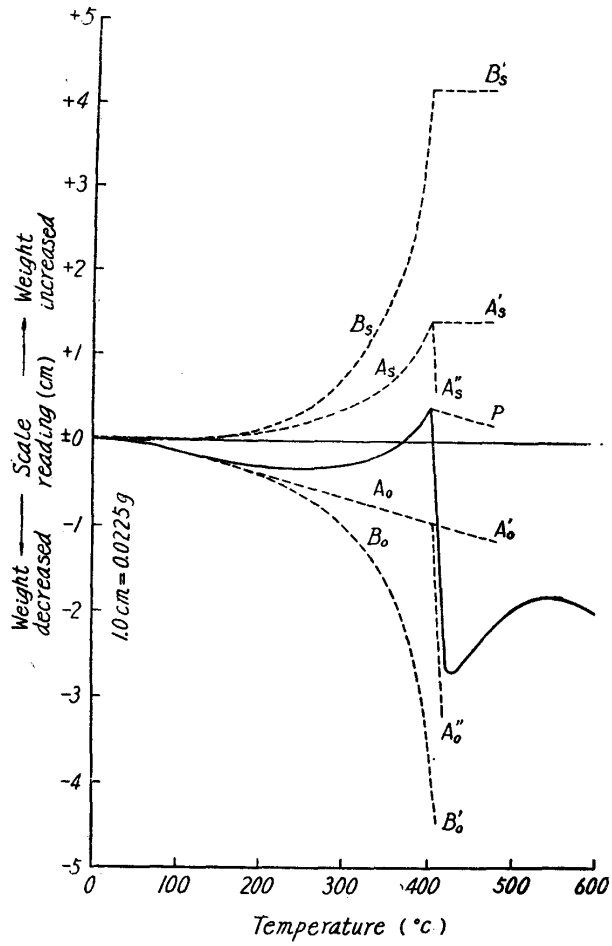

Fig. 1. Analysis of the heating curve of pyrrhotite.

Next, supposing that both the reaction of oxide formation and that of sulphate formation vigorously progressed up to 405°C as indicated respectively by B_0 and B_s lines, let us consider Saito's opinion. In compliance with his opinion, both reactions should progress respectively along B_0' and B_s' lines above 405°C. In this case, the change in weight of ores, that is, the sum of B_0' and B_s' lines must accord with "the first decreasing change in weight". Now, it is noteworthy that the weight of ore again increased remarkably immediately after "the first decreasing change in weight". This phenomenon is inconceivable without supposing the recurrence of the reaction of sulphate formation as well as the interruption of the reaction of oxide formation, which are contradictory to his opinion. Hence, to know the actual processes of the reactions of oxide formation and sulphate

formation, the heating curve of pyrrhotite was experimentaly analyzed from the change of sulphur content of cinder.

Platinum crucible containing exactly 1,000 mg of pyrrhotite particles was suspended in the furnace with a fine string of quartz and was heated at the rate of 2°C/min and the air flow rate of 100 cc/min. As soon as the temperature of the ore reached the prescribed value, the crucible was taken out of the furnace and was left in a desiccator to cool to room temperature. The same experiment was tried five times. Each cinder was mixed after weighing, and total sulphur and sulphate sulphur in it were chemically analyzed. The process of each reaction was indirectly investigated from the changes of the desulphurizing ratio R_{des} and the sulphating ratio R_{SO_4} given by the following formulas:

$$R_{des} = \left(1 - \frac{w \cdot s}{W \cdot S}\right) \times 100,$$

$$R_{SO_4} = \frac{w \cdot s'}{W \cdot S} \times 100,$$

where W and w are respectively the weight of raw ore and that of cinder, and S, s and s' respectively the weight percentage of total sulphur in raw ore, that in cinder and the weight percentage of sulphate sulphur in cinder. The last was determined by a gravimetric analysis of SO_4'' of the sulphate dissolved into a distilled water containing a few drops of the stannous chloride solution, by which the rate of solution of $Fe_2(SO_4)_3$ is accelerated[3]. The sulphate formed in pyrrhotite contains, besides ferrous and ferric sulphate, bassic ferric sulphates, $Fe_2O_3 \cdot 2SO_3$ and $Fe_2O_3 \cdot SO_3$, which are formed by following reactions[4]:

$$Fe_2(SO_4)_3 + Fe_2O_3 = Fe_2O_3 \cdot 2SO_3 + Fe_2O_3 \cdot SO_3$$
$$Fe_2O_3 \cdot 2SO_3 + Fe_2O_3 = 2Fe_2O_3 \cdot SO_3$$
$$Fe_2(SO_4)_3 = Fe_2O_3 \cdot 2SO_3 + SO_3$$
$$Fe_2O_3 \cdot 2SO_3 = Fe_2O_3 \cdot SO_3 + SO_3$$

As they are insoluble in water, all the sulphate sulphurs can not be obtained by the above method. These reactions, however, can be speculated from the change of amount of SO_4'' dissolved in water, and so the present method may be sufficient to know the process of the reaction of sulphate formation.

Fig. 2 shows the changes of the desulphurizing ratio and the sulphating ratio. The former, the reaction curve of oxide formation, inactively progressed at low temperatures, but suddenly became vigorous at 405°C in the same manner as A_0 and A_0'' lines shown in Fig. 1. Consequently, it was experimentally clarified that "the first decreasing change in weight" was due mainly to the vigorous reaction of oxide formation occurring at 405°C but not due to the sintering of ore particles. On the other hand, the latter, the reaction curve of sulphate formation, was discontinuous and the amounts of sulphate greatly decreased for a time at about 405°C. Therefore, the phenomenon showing the decomposition of sulphate also is a cause of "the first decreasing change in weight". As the

(3) J.W. Mellor, *A Comprh. Treatise on Inorg. and Theoret. Chem.*, Vol. XIV, 316.
(4) K. Hirakoso, J. Min. Inst. Japan, **42** (1926), 202.

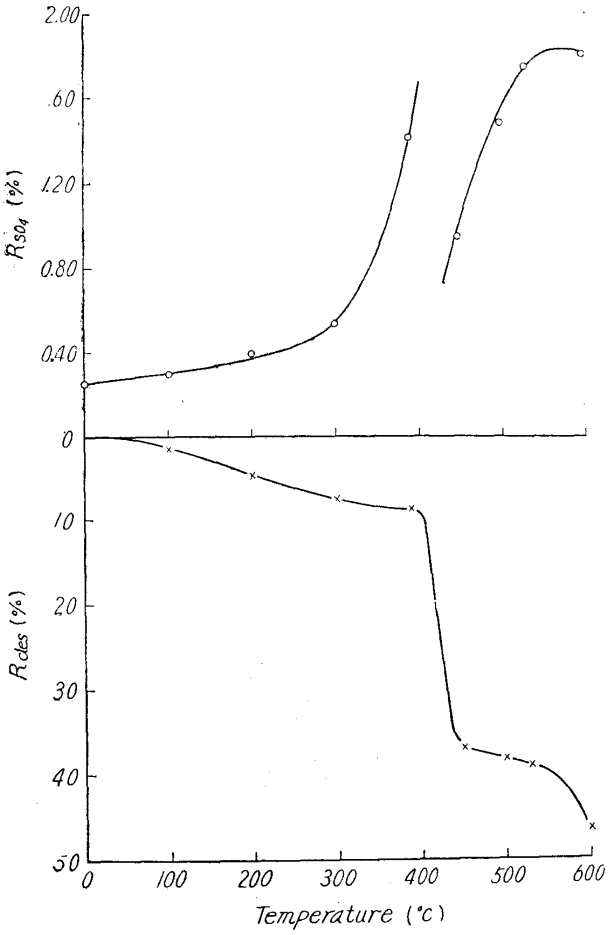

Fig. 2. Reaction curves of the oxide formation and the sulphate formation.

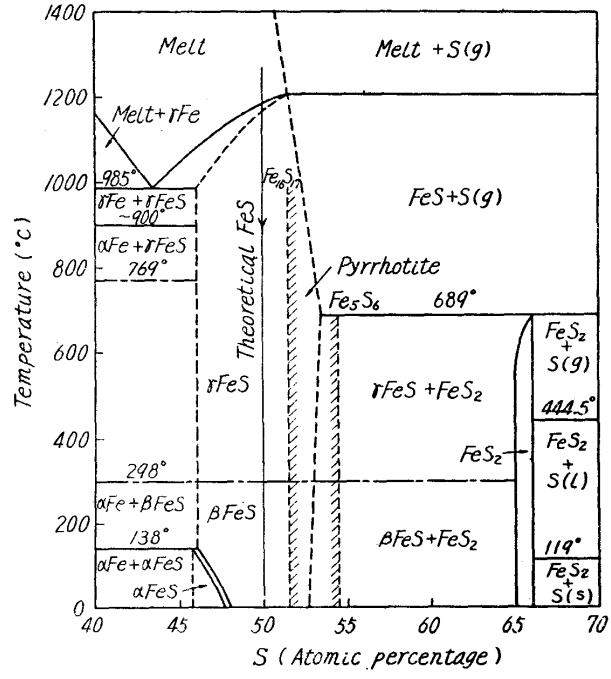

Fig. 3. Equilibrium diagram of Fe-S system.

sulphate is stable at temperatures below 550°C, the decomposition of sulphate is, however, presumed to be a secondary reaction caused by the vigorous reaction of oxide formation. Now, as above mentioned, the reaction of oxide formation again became inactive and that of sulphate formation recurred immediately after "the first decreasing change in weight", and so "the first decreasing change in weight" may be a passing phenomenon. The reason why it takes place only for a time is, however, still an open question.

III. The heating curves of FeS_n

Pyrrhotite has the molecular formula Fe_nS_{n+1} (n=5~16) or FeS_n (n=1.06~1.20), the value n being dependent on the kind of ore. As mentioned in the previous report, the characteristics of the heating curve of native pyrrhotite also are dependent on the kinds of ores. Therefore, the characteristics seem to be associated closely with the molecular formula of ore. When the composition range of pyrrhotite is marked in the diagram of Fe-S system[5], it will be seen that it exceeds the sulphur solubility limit of the solid solution FeS as shown in Fis. 3; in other words, some of ores may contain FeS_2 as a structural component. On the other hand, native pyrrhotite contains chalcopyrite and free sulphur on several occasions. Thus, the sulphur in the ore may exist in the

(5) M. Hansen, *Der Aufbau der Zeitstofflegierungen*, (1936), 726.

following four forms:

1. FeS (solid solution)
2. FeS_2 (a structural component of mixed crystal)
3. $CuFeS_2$ (chalcopyrite)
4. S (free sulphur)

Accordingly, the relations between the characteristics of the heating curve and the forms of sulphur in ore were required to clarify the mechanism of "the first decreasing change in weight".

Table 1. Chemical composition of ores.

Ore	Mine	Component						
		Fe (%)	S (%)	Cu (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	SiO_2 (%)
Pyrrhotite	Ômine	54.40	34.59	0.29	0.08	2.00	0.35	4.79
Pyrite	Hitachi	37.45	43.51	0.22	1.51	0.41	1.48	8.94
Chalcopyrite	Manzô	31.05	34.67	34.21	—	—	—	—
Earth Sulphur	Nishiazuma	1.36	38.21	0.22	0.84	trace	0.28	51.37

First, the heating curve of chalcopyrite produced at the Manzô mine in Miyagi prefecture was studied. The chemical composition of the ore is listed in Table 1. Curve A in Fig. 4 is the heating curve obtained at the heating rate of 2°C/min and the air flow rate of 100 cc/min. It shows a remarkable increase in weight reaching a maximum at about 600°C after a temporary decrease at about 340°C. Curve A′ shows the heating curve obtained at the rate of 10°C/min. H. Saito had reported that the decrease in weight at about 340°C increased with increasing heating rate. In the present careful measurements, however, such an increase was scarcely observed and, moreover, the temperature at which it occurred was about 60°C lower than 405°C. Consequently, the component $CuFeS_2$ in native pyrrhotite may have no connection with "the first decreasing change in weight".

Fig. 5 shows the heating curve of earth sulphur in which the most parts of sulphur exist in free state. The ore used was produced at the Nishiazuma mine in Yamagata prefecture and its chemical composition is

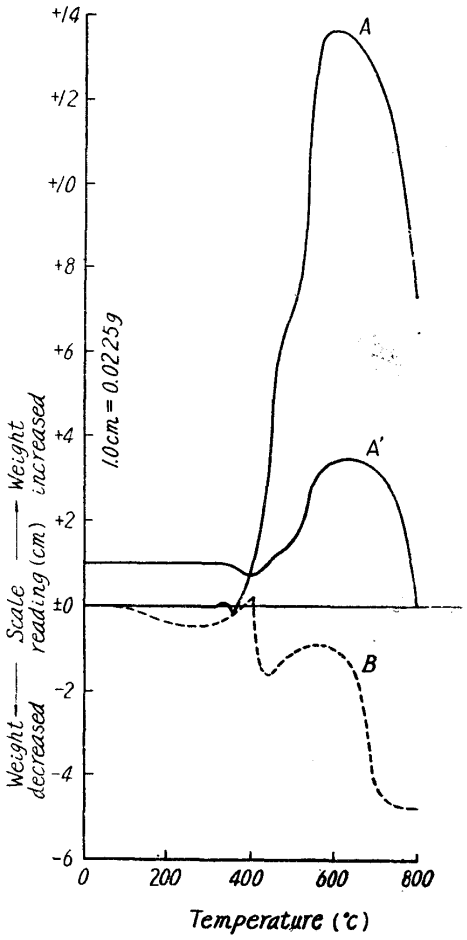

Fig. 4. Heating curve of chalcopyrite.
A : Chalcopyrite—2°C/min
A′: Chalcopyrite—10°C/min
B : Pyrrhotite—2°C/min
1.000 g
100 cc/min

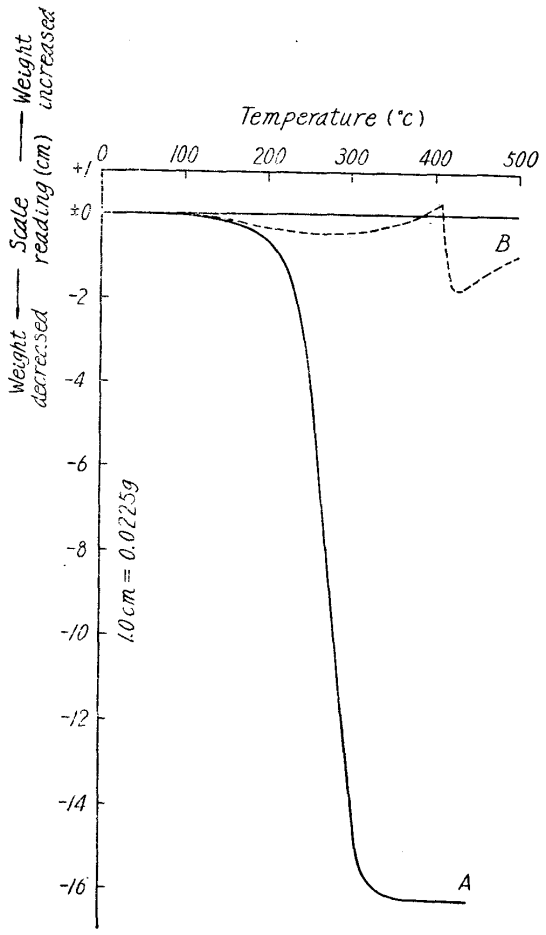

Fig. 5. Heating curve of earth sulphur.
A : Earth sulphur
B : Pyrrhotite
1.000 g, 2°C/min, 100 cc/min.

listed in Table 1. Earth sulphur reacts upon air and lose its weight, generating SO_2 gas. Its reaction became vigorous at about 200°C and almost finished at about 350°C. As this temperature range is considerably lower than that in which "the first decreasing change in weight" takes place, the free sulphur in native pyrrhotite also may have no connection with the phenomenon in question. The initial small decrease in weight observed in the heating curves of various native pyrrhotites is, however, presumed to be due to the oxidation of free sulphur in them.

From these results, "the first decreasing change in weight" is considered to be associated closely with the composition conforming to Fe-S system. Hence, for the purpose of investigating this point, the heating curves of $FeS_{1.04}$, $FeS_{1.08}$, $FeS_{1.14}$ and $FeS_{1.18}$ were exanimed. Among them, the former two are the solid solutions and the others the mixed crystals. These samples were prepared from electrolytic iron powder and purified sulphur powder. The prescribed amounts of both powders were well mixed in an agate mortar and were put in a quartz tube, 20 mm in length. After highly evacuated, this tube was sealed and was put in a furnace. In preparing $FeS_{1.04}$ and $FeS_{1.08}$, the tube was heated at 400, 600 and 800°C for 8 hours and finally at 1,000°C for 20 hours. After cooled to room temperature, the contents were pulverized in an agate mortar. The powders were pressed in steel mould, $5 \times 100\ mm^2$ in section and 10 mm in depth, with the load 30 ton/cm^2, and were put in a quartz tube. After highly evacuated, the tube was sealed and was again heated at 400, 600 and 800°C for 8 hours and finally at 1,000°C for 20 hours. The contents were ground into powders of -200 mesh and were used for the samples. $FeS_{1.14}$ and $FeS_{1.18}$ were prepared from $FeS_{1.08}$ powder and purified sulphur powder by the above-mentioned method. In this case, however, the heating was carried out at 400 and 500°C for 8 hours and 600°C for 20 hours.

Fig. 6 shows the heating curves of samples prepared as above. $FeS_{1.04}$ showed a remarkable increase in weight, that is, the reaction of sulphate formation, from about 200°C to about 550°C, but, in the meanwhile, showed no decrease in weight. Further, the final decrease in weight seen at 800°C was not more than

0.045g (scale reading = −2), and so the reaction rate of oxide formation might be considerably slow. In the case of $FeS_{1.08}$, the increase in weight taking place at temperatures below 550°C became slightly inactive and the final decrease in weight at 800°C increased. Therefore, the combustibility of the ore is presumed to be slightly elevated with the increase of sulphur content. This sample also showed no decrease in weight at temperatures below 550°C. When sulphur content of ore exceeded the solubility limit of the solid solution FeS, a decrease in weight was clearly observed at about 405°C as shown in the heating curves of $FeS_{1.14}$

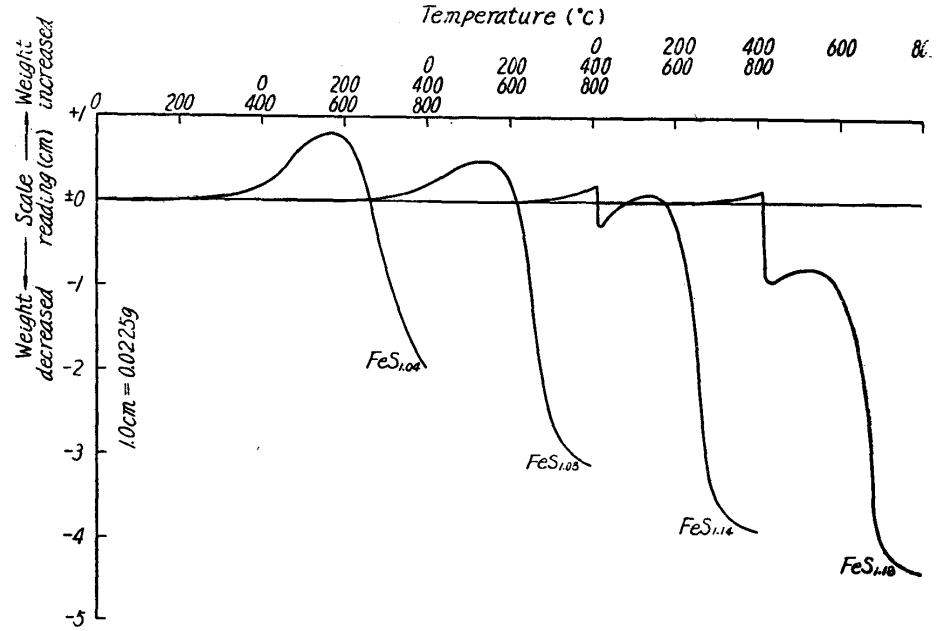

Fig. 6. Heating curves of FeSn.
1.000 g, 100 cc/min, 2°C/min.

and $Fe_{1.18}$. Moreover, the decrease in weight increased with the increase of sulphur content of the ore. The occurrence of "the first decrease in weight" is, therefore, presumed to be due to the deflagration of the component FeS_2. As mentioned in the last report, this conclusion may be convinced by the fact that the temperature causing "the first decreasing change in weight" accords with the igniting temperature of pyrite.

From the above results, the roasting reaction of native pyrrhotite at 405°C or thereabout may be explained as follows: At low temperatures, both the reaction of oxide formation and that of sulphate formation slightly progress, while the component FeS_2 deflagrates at 405°C, generating large amounts of heat of combustion. By this heat evolution, the temperature of the ore will rapidly be raised above 550°C and so the reaction of oxide formation of the component FeS and the decomposition of the sulphate formed at low temperatures will take place, showing a remarkable decrease in weight of the ore. The reaction heat will, however, be absorbed into the furnace before long and these reactions are over, while the reaction of sulphate formation recurrs, showing the increase in weight.

As the ore whose composition is in the range of solid solution does not show

"the first decreasing change in weight" as mentioned, its combustibility may be very low. Removal of such an ore is, therefore, necessary to roast pyrrhotite.

IV. Roasting of the mixture of pyrite and pyrrhotite

From the above results, it was seen that "the first decreasing change in weight" was due to the deflagration of the component FeS_2 in pyrrhotite. Then, the effect of pyrite mixing on the combustibility of native pyrrhotite was investigated. Pyrite used was produced at the Hitachi mine in Ibaragi prefecture and its chemical composition is listed in Table 1.

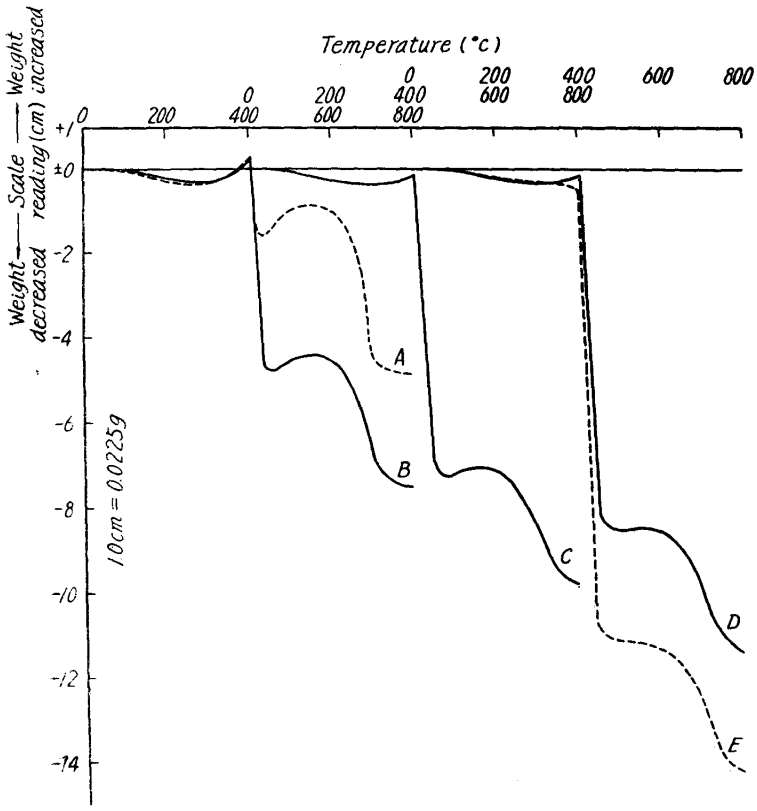

Fig. 7. Heating curves of the mixture of pyrite and pyrrhotite.

A : Pyrrhotite	
B : 25% Pyrite	1.000 g
C : 50% Pyrite	100 cc/min
D : 75% Pyrite	2°C/min
E : Pyrite	

Fig. 7 shows the heating curves of the various mixtures of pyrite and pyrrhotite. The mixing ratios of pyrite were 0, 25, 50, 75 and 100 per cent. From these heating curves, the ratios of the final decreases in weight of the mixtures at 800°C to that of pyrite could be obtained, and their relation to the mixing ratios of pyrite was linear as shown by the line A in Fig. 8. The effect of pyrite mixing on the ignitibility can, therefore, be clearly shown by the ratio of the magnitude of "the first decreasing change in weight" to the final decrease in weight. The Curve B in Fig. 8 shows the relation between it and the mixing ratio of pyrite. In the case of pyrrhotite, the magnitude of "the first decreasing change in weight" was not greater than 35 per cent of the final decrease in weight, while, in the case of 25 per cent pyrite, it rose to 62 per cent at a bound, and in the mixture containing more than 50 per cent pyrite it was comparable well with that of pyrite. It was found that, by pyrite mixing, the ignitibility was elevated greater than a mere mechanical mixing effect. Moreover, the increase in weight taking place immediately after "the first decreasing change in weight" considerably decreased as shown by the Curve C in Fig. 8.

Fig. 9 shows the reaction rate of the mixture at 700°C measured by the change

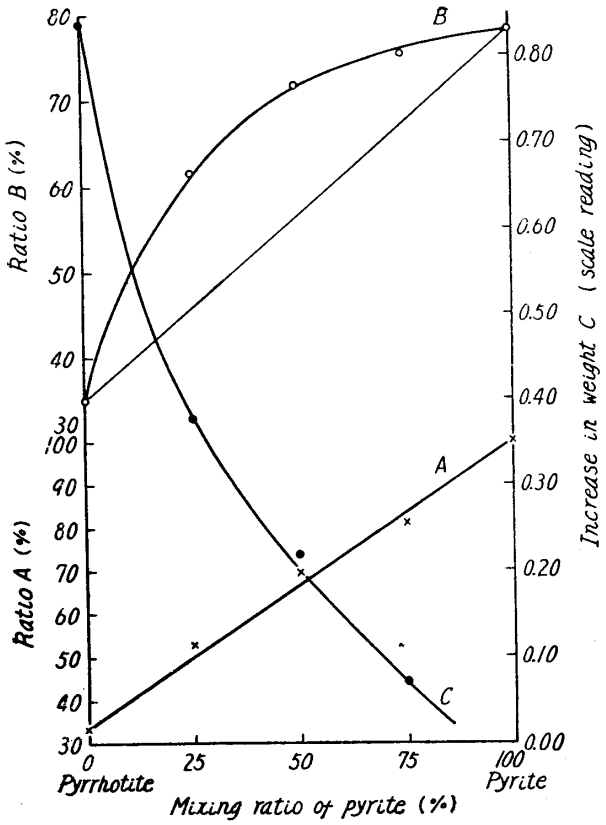

Fig. 8. Effect of pyrite mixing on the ingnitibility of pyrrhotite.

A : The ratios of the final decrease in weight of the mixture to that of pyrite.
B : The ratios of the magnitude of "the first decreasing change in weight" to the final decrease in weight.
C : Increase in weight after "the first decreasing change in weight".

of desulphurizing ratio, from which, the time by which the reaction had progressed to 90 per cent could be obtained. Its relation to the mixing ratio of pyrite is shown in Fig. 10. It was found that by the pyrite mixing the reaction rate of oxide formation also was accelerated greater than a mere mechanical mixing effect. From the various results obtained above, it may be concluded that, with 40~50 per cent pyrite mixing, pyrrhotite becomes roastable under almost the same condition as in the case of pyrite reasting.

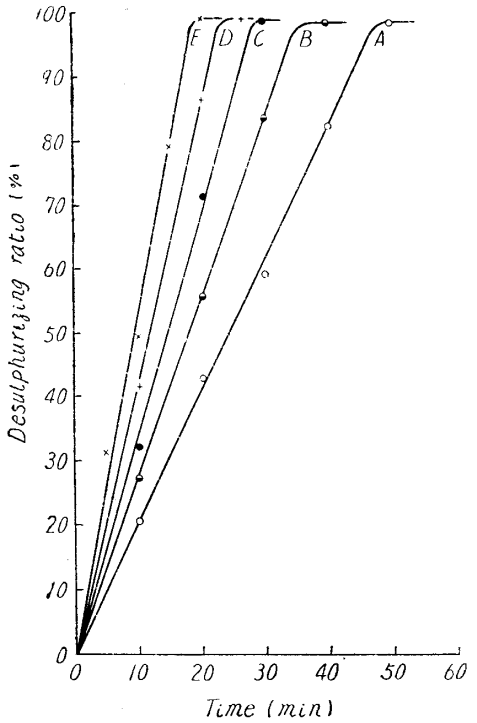

Fig. 9. Reaction rates of mixtures of pyrrhotite and pyrite.

A : Pyrrhotite
B : 25% Pyrite
C : 50% Pyrite
D : 75% Pyrite
E : Pyrite
700°C

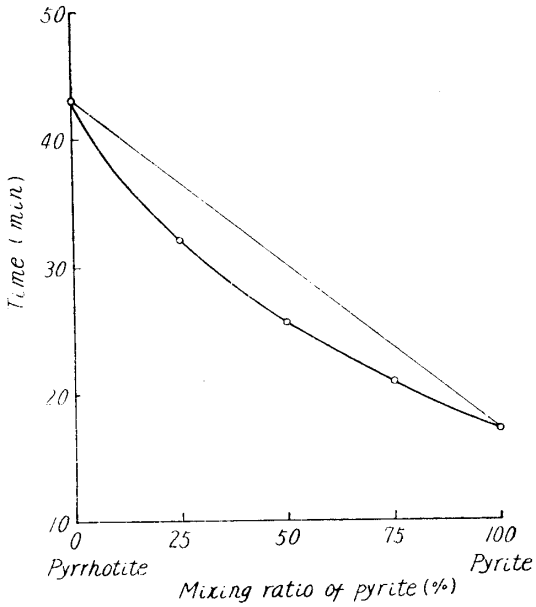

Fig. 10. Effect of pyrite mixing on the reaction rate of pyrrhotite.

Summary

The results obtained may be summarized as follows:

(1) Pyrrhotite of the chemical composition in the range of solid solution did not show "the first decreasing change in weight", while the ore of the chemical composition in the range of mixed crystal clearly showed it. Hence, the phenomenon was presumed to be due to the deflagration of the component FeS_2 of the ore.

(2) The deflagration of FeS_2 in ore led to the reaction of oxide formation of the component FeS and the decomposition of the sulphate formed at low temperatures. The magnitude of "the first decreasing change in weight" was, therefore, larger than the decrease in weight resulting from the oxidation of FeS_2.

(3) By pyrite mixing, the combustibility of pyrrhotite was remarkably elevated greater than a mere mechanical mixing effect.

(4) With 40~50 per cent pyrite mixing, pyrrhotite may become roastable under almost the same condition as in the case of pyrite roasting.

Acknowledgement

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